

# Photon-blockade induced photon anti-bunching in photosynthetic Antennas with cyclic structures

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One of the important nonclassical effects in quantum optics is the anti-bunching, which has been observed in a large class of physical systems - including light-harvesting antennas with cyclic structures. The units of the ring couple with adjacent ones through dipole-dipole interactions. We show how this strong dipole-dipole interaction leads to photon-blockade resulting in the suppression of double excitation pathway and anti-bunching in photosynthesis systems. The robustness of the photon blockade is demonstrated against the disorder in the ring structures. We hypothesize that the effect may be utilized by light-harvesting systems to avoid damages from excess energy.

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The solar radiation is an abundant, clean, and sustainable source for our energy needs in conceivable future [1, 2]. Promising methods of harvesting sunlight are to utilize the biological light-harvesting machinery [1–3], or combined technology [4, 5] of bio-organic and nanomaterial design. To pursue these new methods, it requires to understand the underlying design principles of both the high quantum efficiency [6–8] as well as the protection mechanism against damage by excess energy [9] in the natural light-harvesting complexes in photosynthetic system. Many efforts have been put together recently to unveil these design principle from optical properties of individual pigment-complexes [10–14], and the structural organizations among complexes [15–21]. One prominent discovery is symmetric structures in the light-harvesting complexes [22]. For example, the light harvesting complexes II (LHCII [17]) of the green plant antenna, has a  $C_3$  symmetry in the photosystem II (PSII), while light-harvesting antennas (LHI and LHII [23–26]) in the purple bacteria exhibit a  $C_8$  symmetry, despite small disorders.

On the other hand, anti-bunching of photon statistic is an iconic quantum optical phenomena in atomic ensembles, cavity-atom, and artificial structures [27–34]. In natural light-harvesting systems, the anti-bunching was reported [35] in the resonance fluorescence from LHI. It was explained as a collective behavior [35] of the whole ring. The single molecular fluorescence experiment [13] on the artificial synthetic  $\pi$ -conjugated spoked-wheel also reported a similar effect. Benefiting from the recent progress of surface-enhanced spectroscopy, van Hulst et.al has successfully measured the resonance fluorescence from a single LHII [14]. An anti-bunching was reported in the second-order correlation of resonance fluorescence. A mechanism of exciton-exciton annihilation (EEA) [36] is proposed to account for the dip of fluorescence at zero time delay. However, quantum optics studies [29, 37] suggest that other possibilities cannot be ruled out. In this letter, we propose photon-blockade mechanism to

account for the observed phenomena instead of the two-excitation annihilation originally suggested in Ref. [14]. We also suggest that the two mechanisms may be distinguished through a temperature-dependent experiment [38].

We consider a generic ring structure ( $N$  pigments), wherein the interaction between chlorophylls is characterized by hopping of excitation with strength  $J$ . The configuration is shown in Fig. 1 (a), where  $N$  chlorophylls are organized evenly on a ring. And the energy levels ( $|e_i\rangle$  and  $|g_i\rangle$ ) are illustrated for the  $i$ th-chlorophyll in the subset of Fig. 1(a). The Hamiltonian reads

$$H_0 = \sum_{i=1}^N \omega_i s_i^z + \sum_{i=1}^N J_i (s_i^+ s_{i+1}^- + s_{i+1}^+ s_i^-), \quad (1)$$

where  $s_i^+ = |e\rangle_i \langle g|$ ,  $s_i^- = |g\rangle_i \langle e|$ , and  $s_i^z = \frac{1}{2}(|e\rangle_i \langle e| - |g\rangle_i \langle g|)$  with  $|e\rangle_i$  ( $|g\rangle_i$ ) as the two electronic levels on optical resonance with a laser drive field or sunlight. The hopping of excitation is induced by the dipole-dipole interaction [39] between chlorophylls, namely  $J_i = \langle e_{i+1} g_i | V | g_{i+1} e_i \rangle$ , with

$$V = \frac{\mu_{i+1} \cdot \mu_i - 3(\mu_{i+1} \cdot \vec{e}_{R_{i,i+1}})(\mu_i \cdot \vec{e}_{R_{i,i+1}})}{|\vec{R}_{i,i+1}|^3}, \quad (2)$$

where  $\vec{R}_{i,i+1}$  is relatively position between  $i$ -th and  $(i+1)$ -th chlorophylls and  $\vec{e}_{R_{i,i+1}} = \vec{R}_{i,i+1}/|\vec{R}_{i,i+1}|$ . For the interaction, we consider the fact that the distance between chlorophylls is far smaller the absorption wavelength namely,  $|\vec{R}_{i,i+1}| \ll \lambda$ , where  $\lambda$  is the absorption wavelength [39]. Typically, the radius of the ring is about 4-5nm for light-harvesting complexes [14] and 6nm for the synthetic macro-molecule [13], which is far smaller than the corresponding absorption wavelength, 800nm [14] and 465nm [13]. We consider in current model only the nearest neighbor interaction between chlorophylls [40].

For a uniform ring ( $\omega_i = \omega$ ), the non-perturbative Hamiltonian  $H_0$  can be diagonalized via Jordan-Wigner

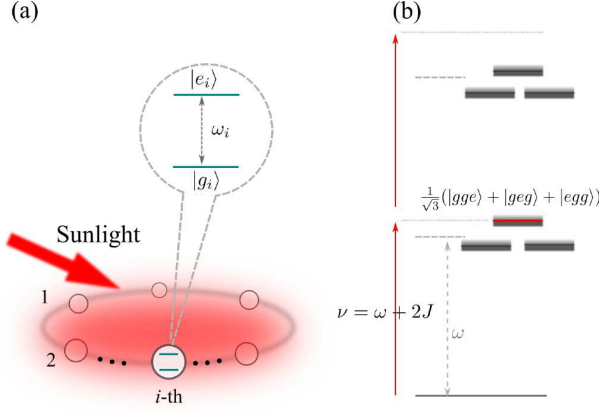


Figure 1. ( Color online ) (a) Generic ring with  $N$  chlorophylls. (b) Example of energy-levels with  $N = 3$ . The dashed lines show the energy levels, equally spaced with  $\omega$ , for a ring without inter-chlorophylls interaction. The solid lines with shadow represents the energy levels for the same ring with dipole-dipole interaction.

transformation [41], where the eigen-system are divided into two categories: odd and even excitation. The eigen-energies of single and double excitation states, relative to the ground state with all molecules on ground states, are given by

$$E_s(k) = \omega + 2J \cos 2\pi k/N, \quad (3)$$

and

$$E_d(k_1, k_2) = 2\omega + 2J[\cos 2\pi(k_1 + 1/2)/N + \cos 2\pi(k_2 + 1/2)/N], \quad (4)$$

where  $k, k_1$  and  $k_2 \in \{0, 1, 2, \dots, N-1\}$ , and  $k_1 \neq k_2$ . The energy spectrum for a simple case  $N = 3$  is shown in Fig. 1(b). The energy levels of both single-excitation in Eq. (3) and double-excitation in Eq. (4) are shifted due to dipole-dipole interaction between chlorophylls. In current model, we have assumed all transition dipoles are parallelly pointing up. This assumption results in a positive coupling strength  $J > 0$ . For real case of LHI's B800 ring with dipole moments slightly slanted, the coupling is negative. However, the following discussion of off-resonance is still valid. For the case  $J > 0$ , the highest energy level ( $k = 0$ ) of single excitation subspace is  $|\psi_s\rangle = 1/\sqrt{N} \sum_{i=1}^N |g_1 g_2 \dots e_i \dots g_N\rangle$ , which is a single-photon superradiance state. One important feature is that the amount of energy shift of the superradiance state is larger than that of highest double-excitation state, as shown in Fig. 1(b). The transition dipole moment from the ground state to this symmetric state is enhanced by a factor of  $\sqrt{N}$ , while the transition dipoles for other states essentially vanish. Such vanishing of transition dipole moment leads to the subradiance states [42, 43], whose radiation decay rate is significant suppressed. The direct result of the symmetric structure is the enhancement of transition amplitude from the ground state to

the symmetric state, while transition to other states are canceled or suppressed. This feature is also known as super-absorption [26, 39, 44].

As for absorption, we consider the interaction of driving light field with ring structures. With this observation, we assume all the chlorophylls couple uniformly to the incident light, and simplify the interaction of ring with driving field as

$$H_I = \sum_{i=1}^N \Omega_R (s_i^+ e^{-i\nu t} + s_i^- e^{i\nu t}), \quad (5)$$

where  $\Omega_R$  is the Rabi frequency associated with coupling of photon mode with frequency  $\nu$  to the atomic transition  $|g\rangle \rightarrow |e\rangle$ .

The ring structure also interacts with the surrounding vacuum field, which results in dissipation of excitation in the system. The dissipation dynamics is described by the master equation as follows [37, 45, 46]

$$\frac{\partial \rho}{\partial t} = -i[\rho, H] - \frac{\gamma}{2} \sum_{ij} (s_i^+ s_j^- \rho + \rho s_i^+ s_j^- - 2s_j^- \rho s_i^+), \quad (6)$$

where  $\gamma$  is dissipation strength, and  $H = H_0 + H_I$  is the total Hamiltonian. Equation (6) was used to show the collective spontaneous emission, known as the Dicke superradiance [46]. In the current discussion, we neglect collective the Lamb shift [47] in the master equation.

To demonstrate the new mechanism, we mainly focus on calculating the probability of having double excitations in this ring structure. Experimentally, the method to determine the number of excitations in a single aggregate is to measure the multi-order correlations of the resonance fluorescence [37]. To check the probability of double excitations, we typically measure the second-order correlation. The measured signal is presented by a normalized second-order correlation function [48], defined as

$$g^{(2)}(t, \tau) = \frac{\langle S^+(t) S^+(t+\tau) S^-(t+\tau) S^-(t) \rangle}{\langle S^+(t) S^-(t) \rangle \langle S^+(t+\tau) S^-(t+\tau) \rangle}, \quad (7)$$

where  $S^\pm = \sum_{i=1}^N s_i^\pm$ . The correlation function quantifies the probability of having one photon emitted subsequently at time  $t + \tau$ , after an initial photon already emitted at time  $t$ . A lowing emission probability at  $\tau = 0$  indicates a suppress of the probability having double excitation in the system.

In Fig. 2, we show the normalized second-order correlation  $g^{(2)}(\tau) \equiv g^{(2)}(t, \tau)$  as a function of delay time  $\tau$  at steady state ( $t \rightarrow \infty$ ) for the ring structure with (blue solid curve) and without (black dashed curve) interaction between adjacent chlorophylls. The correlations are plotted for rings with 3 and 8 chlorophylls, respectively in subfigures (a) and (b). The parameters using in the simulation are estimated from LHI in the purple bacteria [40, 49], where  $J = \omega/10$  and  $\gamma = J/10$ . We also

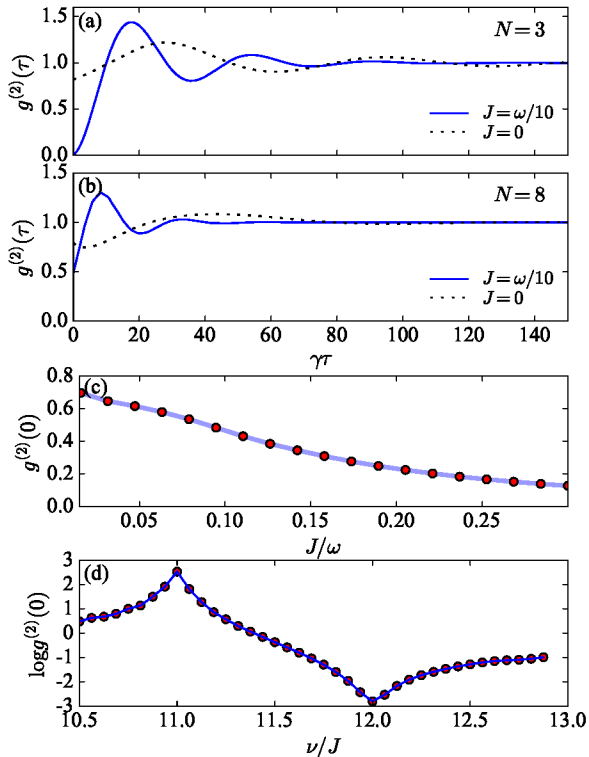


Figure 2. (Color online) The second-order correlation functions for system with (blue solid line) and without dipole-dipole interaction (black dashed line). The correlations are plotted for the ring structures with (a)  $N = 3$  and (b) 8 chlorophylls. (c) The second-order correlation at  $\tau = 0$  is plotted as a function of the strength  $J$  of the dipole-dipole interaction for the ring with 8 chlorophylls. (d) The second-order correlation at  $\tau = 0$  is plotted as a function of the laser frequency  $\nu$  for the ring with 3 chlorophylls.

assume relatively weak driving field  $\Omega_R = \gamma$ . At  $\tau = 0$ , it shows a significant reduction of the amplitude of emitting two photons simultaneously, in comparison with the one without interaction. This phenomena is known as anti-bunching effect, which can be explained with the energy-level scheme in Fig. 1(c). Due to the dipole-dipole interaction between adjacent chlorophylls, the energy for symmetric superadiance state  $|\psi_s\rangle$  is shifted to  $\omega + 2J$ . The interaction with incident light in Eq. (5) can only induce the transition from the ground state to this superadiance state, if the transition dipoles of individual chlorophylls are aligned along the same direction. The probability of exciting the system from superradiance state to all double-excitation states are suppressed, since a second photon with the same energy  $\omega + 2J$  is far detuned from resonance with the transition from the superradiance state to the double excitation eigenstates under the condition of strong dipole-dipole interaction. In Fig. 2(c), we show effect of increasing coupling constant  $J$  on the correlation function at zero delay. The curve shows an enhancement of blockade with a decrease of

emission rate[33], due to increasing detuning with larger interaction strength. The anti-bunching depends intensively on how the driving field is tuned. In Fig. 2(d), we show the correlation function  $g^{(2)}(\tau = 0)$  as a function of laser frequency  $\nu$  for the ring with  $N = 3$ . The dip on the curve shows the anti-bunching in resonance fluorescence ( $\nu/J = 12$ ), while the peak illustrates photon bunching ( $g^{(2)}(\tau = 0) > 1$ ) under the two-photon resonance ( $\nu/J = 11$ ) with the transition from the ground state to double-excitation state. This feature is unique to the photon-blockade mechanism, and can be utilized to distinguish the current mechanism from EEA.

The current mechanism is also an analogy to photon-blockade effect of a single atom in a cavity [29], where the interaction between the cavity mode and the single atom tune all the double-excitation states off-resonant with the incident photon. Instead of a single atom [50], we show that collective modes of the ring result in a similar effect of reducing double excitations. The collective effects also play an important role in Rydberg blockade[30–32]. The observed anti-bunching in resonance fluorescence in Ref. [14] was originally attributed to the annihilation of two single excitations. However, we show a rather simple origin of the anti-bunching in the emitted photon statistics, based on the simple observation from cyclic structures. In principle, both EEA and photon-blockade could be responsible for anti-bunching a given experiment. The current mechanism has not exclude the EEA mechanism, since photon-blockade mechanism just reduces the rate of double excitation and EEA may take role when double excitation is accidentally created.

The current mechanism could be beneficial in light-harvesting processes. The sunlight energy is mainly absorbed by chlorophylls in these antenna complexes [22]. An excess of energy will produce an accumulation of excited chlorophylls; which further result in triplet chlorophylls[51] and eventually oxidatively damage chlorophylls[52–54]. The blockade mechanism reduces the probability of two excitations that appears in the antenna rings, and in turn, separate the output of excitons in time as sequence. Under this observation, we hypothesise the photon-blockade as a new mechanism in light-harvesting system to protect the apparatus from oxidative damage due to excess photons. The blockade mechanism acts as an additional layer of protection of chlorophylls by reducing the probability of two excitations in one antenna ring. We remark that the blockade of photon absorption reduces the probability of double excitations, however, does not exclude the double excitations.

We have illustrated the mechanism of blocking double excitations in the cyclic structure with very high degree of symmetry ( $D_N$ ). However, the variation of protein environment results in inhomogeneous broadening (static disorder) and dynamical fluctuation to both chlorophyll transition energies  $\{\omega_i\}$  and inter-chlorophyll

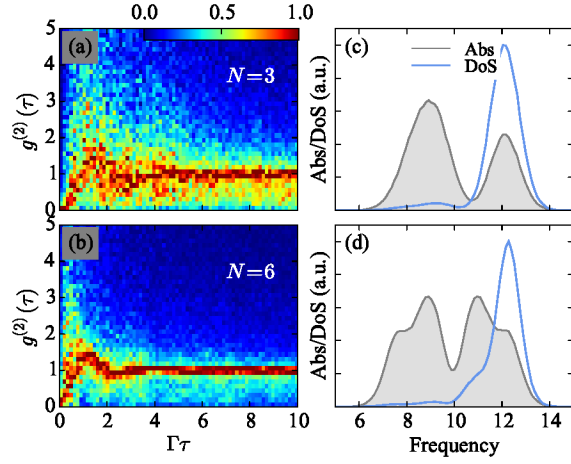


Figure 3. (color online) Distribution (a, b) of the second-order correlation  $g^{(2)}(\tau)$  in ensemble system with disorder of both chlorophyll transition energy  $\{\omega_i\}$ , and the corresponding linear absorption and density of states for  $N = 3$  and  $N = 6$ .

hopping strength  $\{J_n\}$ . It was already proved that the inhomogeneous broadening of transition energies  $\{\omega_i\}$  is the main contribution of line-width in absorption spectra of cyclic structures [40]. As shown below, the inhomogeneous broadening simply induces a distribution of second-order correlation function with the central line matching that of homogeneous ring. The inclusion of disorder of inter-chlorophyll coupling only further broadens the distributions. In current study, we will focus on the transition frequency disorder  $\omega_i$ . To consider static disorder, we set the transition frequency  $\omega_i = \omega + \delta\omega_i$ , where  $\delta\omega_i$  is the variation of transition energy on  $n$ -th chlorophyll. In our simulation, we choose a Gaussian distribution for the disorder [55], namely,

$$p(\delta\omega_i) = \frac{1}{\sqrt{2\pi}\sigma_\omega} \exp\left[-\frac{\delta\omega_i^2}{2\sigma_\omega^2}\right]. \quad (8)$$

We examine the second-order correlation of the cyclic structures ( $N = 3$  and  $N = 6$ ), with the disorder [56]  $\sigma_\omega = \omega/10$ . The distribution of the second-order correlation is calculated by sampling of the chlorophyll transition frequencies  $\{\omega_i\}$  on different chlorophylls on the ring.

Fig. 3(a) shows the density plot of correlation function distribution with the chlorophyll-energy disorder on a ring with  $N = 3$  chlorophylls with inter-chlorophylls dipole-dipole interaction. The distribution is generated with 1000 sets of energy configuration  $\{\omega_i\}$ . Even with disorder, the plot for system with dipole-dipole interaction shows a prominent suppress of two photon emission at  $\tau = 0$ . Fig. 3(c) shows the corresponding linear absorption spectra (blue solid line) and the density of state (gray dashed line). The main peak of the absorption spectrum corresponds to the transition from the ground

state to the superradiance state. The absorption of other states are suppressed due to the effective weak transition dipole, despite larger density of state, shown in Fig. 3(c). We remark that the higher peak on the curve of DoS in Fig. 3(c) is caused by a two-fold degeneracy of states. The degeneracy is illustrated in Fig. 1(b).

In Fig. 3(b), we present the correlation function  $g^{(2)}(\tau)$  distribution for a ring with  $N = 6$  chlorophylls. The distribution shows similar behavior of suppressing simultaneous two-photon emission as that of the ring with 3 chlorophylls. Comparing to that with  $N = 3$  chlorophylls, the suppressing of double excitation on the ring is significantly reduced. It was shown that the dense pack of  $N$  chlorophylls into unit, smaller than the wavelength it absorbs, increases the cross section of absorbing photons through similar mechanism of superradiance. However, we show that the advantage of increasing number of chlorophylls is trade-off by a increasing the probability of damage, due to the loss of photon-blockade. Such observation suggests a competing factor, which could be utilized to understand optimal numbers [18] of pigments in cyclic antennae structures. Another factor is the pure dephasing rate, due to the dynamical fluctuations of transition energies. It is known [57] that the anti-bunching effect is less sensitive to the pure dephasing rate [58].

We have demonstrated the mechanism of photon-blockade with the generic model of ring structures under a single mode driving field. Replacement of single mode driving field by sunlight is challenging. This is because of the broadband nature of sunlight and we need to drive the coefficients of one- and two-photon absorption processes for the ring with strong dipole-dipole interaction.

In conclusion, we have introduced an alternative mechanism - photon-blockade, which can result in the anti-bunching effect in resonance fluorescence from natural light-harvesting antennas with cyclic structures, where each unit has moderate interaction to adjacent ones. This mechanism can be utilized to explain the anti-bunching behavior observed in the very recent single-molecule resonant fluorescence experiment on LHII, where it was speculated as indication of double-excitation annihilation [14]. We further demonstrated the robustness of the blockade mechanism against the inter-chlorophylls disorder, which dominantly contributes to the line-width of absorption of light-harvesting complexes.

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